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**ENVIRONMENTAL MANAGEMENT PERSPECTIVES
OF SOIL FLUORIDE IN NEW ZEALAND'S AGRICULTURAL SOILS**

A thesis presented in partial fulfilment of the requirements for the degree of

Master in Environmental Management

at the Institute of Agriculture and Environment,
Massey University, Palmerston North, Manawatu, New Zealand

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2017

*To the people running in my veins,
And to those who made an impact in my life, here and there*

Abstract

The prolonged use of phosphate (P) fertilisers has inherited an accumulation of F in topsoils and it is considered to be building up in most of New Zealand's (NZ) agricultural soils. New Zealand research into soil F has been hampered by the lack of a reliable and simple test for soil F. The accuracy of different methods to quantify the presence of F in analytical preparations is dependent on interfering elements such as the aluminium (Al) content of the sample. The conventional methodology of NaOH fusion with an ion-specific electrode method is considered to be time consuming, expensive and very dependent on the abilities of the operating technician, thus it is not ideal for environmental monitoring.

To improve the traditional method, an alternative technique to the standard fusion protocol was developed by the Fertilizer & Lime Centre Research (FLRC), Massey University, and that found that simple extraction of soil with dilute sodium hydroxide four molar (NaOH 4M) consistently reported 80% of the total soil F across volcanic soils. The initial FLRC initial work was further examined in this research to confirm the repeatability of the NaOH extraction technique to quantify soil F in a range of NZ soil orders. Also, to assess the relative accuracy of the NaOH extraction technique across different NZ soil orders by comparing different NaOH concentrations.

The main aim was to compare different methods and NaOH concentrations to determine total soil F on a representative range of soil orders collected from 13 agricultural sites with a long-term P fertiliser application background. The variability between soils orders was assessed as a function of soil properties. Furthermore, microbiological analyses were performed to assess the impacts of total F, as determined by NaOH extraction method, on soil microbial activity. This study also provides a discussion on the environmental management implications of the emerging F issue in the NZ pastoral land.

The total soil F concentration across seven different soil orders ranged between 152 mg F kg⁻¹ and 708 mg F kg⁻¹. The NaOH extraction method showed significant correlation with the alkali fusion/ISE technique ($r > 0.92$). The accuracy of the F determination is very dependent on interfering elements such as Al/Fe oxy-hydroxide content, and NaOH 10M extraction method showed the lowest variation within allophane-rich soils compared to the 4M and 16M extractions. Results suggest that the NaOH 10M method can be used for wide-scale

environmental studies and monitoring programmes across a variety of New Zealand soils, particularly for Allophanic soils.

A significant correlation was found between dehydrogenase enzyme activity (DHA) and the labile or total Al and Fe content ($r > 0.82$), whereas the microbial biomass carbon (C_{mic}) was positively correlated with the non-labile Al and Fe fraction in soils ($r > 0.89$). These findings indicate that these microbial parameters can be used for environmental monitoring programmes. The DHA can be used to assess the effects of the labile F to microorganisms and the C_{mic} variable could be used as an indicator of the total F effects to livestock.

Acknowledgements

Above all, the love I share with the ones I care for is my one and only provider of all, without this source, nothing would have been possible so far in my life.

To my beloved family: Marta, Marce, Milu, Olivia, Sam and Fabi, endless thanks for your love and support, despite the distance I've always felt you close. To my grandfather, Piito Jover, who has always shown strength and perseverance and taught us how to keep things simple in life. Special mention goes to my recently passed away grandmother, Ropi Rahal, who made a huge impact on my life, and to whom I owe my passion for cook and travel.

I thank my supervisor, Dr Chris Anderson, for helping me conclude this thesis and for his support. Also, I thank my co-supervisor, Dr Paramsothy Jeyakumar, for his patience and guidance during my laboratory and data workings.

To the Ministry of Foreign Affairs and Trade (MFAT) for giving me the unique opportunity to study a higher education degree overseas by awarding me with the New Zealand Development Scholarships (NZDS). It has been one of my best experiences and New Zealand will remain in my heart forever.

To the Fertilizer & Lime Research Centre (FLRC), Massey University for supporting this project. To the international student support office (ISSO) staff at Massey University, for always disperse my worries and doubts, and giving me the support I needed every time I run to their office looking for help and advice, especially Jamie Hooper.

Also, my appreciation to Dr Mike Bretherton for his contribution to the soil description section for this study and to Matthew Taylor for his collaboration on providing very useful information on soil fluoride.

To the Institute of Agriculture and Environment staff, the soil science laboratory staff at Massey University and to the postgraduate students who offered their support during my laboratory work and helped me with sampling or clarifying some uncertainties. Each one of you helped me somehow to conclude this work: John Holland, Karen Hytten Ian Furkert, James Hanley, Glenys Wallace, Bob Toes, Quang Mai, Ross Wallace, Peter Bishop, Geretharan Thangavelautham, Grace Chibuike, Roberto Calvelo, Kamal Prasad, Aaron Stafford and Hadee Thompson-Morrison.

I am deeply grateful to Stefanía Romero and Julia Bohórquez for their input and time to read and discuss my work. Also, to Aniek Hilkens and Florentine van Noppen who made things much easier during the struggle. To my friends and the 92 Wood St family, my sincere thanks for your daily encouragement, patience, honesty and love, your hugs and smiles made all the difference. I will always carry you all in my heart. And finally, to friends in Paraguay, Dulce, Fede and Ayi for their words of alleviation, care and affection. You all contributed in relieving some of my stress out and cheered me up to get the confidence I needed to finish my studies.

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